Structure of Low Pressure Premixed Methane Flames Inhibited with CHF_3 and C_3HF_7[*]

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We have studied changes in flame structure of low pressure premixed methane/oxygen flames as they are inhibited by the fluorinated halon replacement agents CHF_3 and C_3HF_7 (HFC-227ea). We have measured temperature and intermediate species profiles in both inhibited and uninhibited flames. In the case of CHF_3, the measurements on flame structure are compared to calculations performed with the Sandia PREMIX code, using the kinetic mechanism recently developed at NIST for the combustion of C_1 and C_2 fluorocarbons. A primary purpose in conducting these studies is to provide experimental data for validation of these kinetic models, since comparatively few studies of the detailed flame structure of these systems have been performed to date, and many important reactions have not been thoroughly studied experimentally.

Experiments were performed using a McKenna burner 6 cm in diameter operated with a premixed flame of methane and oxygen having an equivalence ratio of unity. The flame pressure was maintained at 10 Torr, and a co-flow of argon having an identical mass flux surrounded the premixed gases. To this base flame were added two fluorinated suppression agents: CHF_3 and C_3HF_7. Heptafluoropropane was added in quantities up to 4% of the total flow rate of methane and oxygen (in four increments), while trifluoromethane was added up to 8.8% of the total. The relative proportions of the two dopants were chosen to achieve equal loadings of F atoms. The addition of the two agents made the overall flame stoichiometry slightly fuel rich, raising ϕ to 1.07 in the case of CHF_3, and 1.09 for C_3HF_7.

Temperature profiles of both the inhibited and uninhibited flames were recorded using a type R (Pt. vs. Pt/13% Rh) thermocouple, having a wire diameter of 0.08 mm. The thermocouples were coated with alumina to avoid catalytic activity in the flame zone. The ceramic coating was reasonably stable in the fluorinated environment, surviving for several hours without noticeable decomposition. A radiation correction was determined by making comparisons with a reference flame whose temperature has been previously measured by LIF of OH. The magnitude of the correction was approximately 300K at the peak temperature region of the uninhibited flame.

Profiles of intermediate species were recorded using laser-induced fluorescence. An excimer-pumped dye laser was used to excite fluorescence, which was collected at right angles by a photomultiplier using appropriate bandpass filters. Background flame emission was also collected in the same way. Irises on the incoming laser beam and at the focal point of the collection optics gave a spatial resolution of 0.5-1 mm.

As the agents were added, the methane/oxygen flame became noticeably more luminous and the emission zone moved further from the burner, from about 8.5 mm in height in the uninhibited flame, to about 10.5 mm when either 8.8% CHF_3 or 4% C_3HF_7 was added. The increase in standoff distance with the addition of the agents is consistent with the expected decrease in flame speed. The amount of flame emission from both CH (recorded at 430 nm) and C_2 (recorded at 516 nm) increased by a factor of seven when 4% C_3HF_7 was added. Addition of 8.8% CHF_3 produced about half as much CH emission as 4% C_3HF_7. These observations indicate that the fluorine chemistry has a substantial effect on the reactions leading to chemiluminescence.

Compared to the uninhibited flame, the temperature profiles of the inhibited flames have a slower rise above the burner surface, but reach a peak temperature some 100K higher. Temperature profiles of the two inhibited flames are almost identical. Since the relative loadings of the two agents were chosen to provide equal numbers of fluorine atoms, this close coincidence of the temperature profiles indicates that, for agents with a high fluorine/hydrogen ratio, the inhibition depends primarily on the number of fluorine atoms added to the flame, rather than on the structure of the agent or the initial reaction pathways.

We are currently studying LIF profiles of several species, fluorine-containing as well as those present in the uninhibited flame. The profiles of these intermediates gives a further indication of flame structure. The profile of the CH radical, for instance, moves about 3 mm further from the burner as C_3HF_7 is added up to a mole fraction of 4%. Unlike the emission from excited state CH, which increases dramatically as the agents are added, the ground state CH concentration only increases by about 20% upon the addition of 4% C_3HF_7.

To interpret the flame studies, we have performed flame structure calculations using the fluorocarbon reaction mechanism recently developed at NIST. The reaction set as it currently exists includes all fluorinated methane derivatives, but not any C_3 species such as heptafluoropropane. The calculation was performed using the measured temperature profile. The predicted location of the ground state CH peak is at 13 mm above the burner, about 4 mm higher than the location experimentally observed. In the uninhibited flame, the predicted and observed locations of the CH peak lie within 1 mm of each other. This predicted change in flame standoff distance is primarily a result of the fluorocarbon kinetics, not the altered temperature profile. Performing a calculation on the uninhibited flame, but using the temperature profile of the inhibited flame, shifts the CH location by less than 1 mm.

This disagreement in the profiles of the inhibited flame indicates that the mechanism significantly overpredicts the effect of CHF_3 on the flame speed, at least under the the current conditions of pressure and composition. Among the possible causes for the discrepancy is the behavior of COF_2, which is a relatively stable species predicted to slowly react with H atoms to form HF. Since HF formation is primarily responsible for the reduction in the number of atomic hydrogen when the agent is added, a slower removal rate for COF_2 would mean that fewer H atoms could be removed, and thus the flame speed would not be reduced as significantly. The removal reactions of COF_2 are not well investigated experimentally, and so the behavior of this species in these flames may allow the kinetics to be optimized to better predict the observed behavior of these agents.